1986

IUPAC 7th International Symposium on Cationic Polymerization and Related Processes

Otto Vogl
University of Massachusetts - Amherst, vogl@polysci.umass.edu

Dietmar Lohmann

Dietmar Lohmann and Otto Vogl, *IUPAC 7th International Symposium on Cationic Polymerization and Related Processes,* Polymer News, 11(12), 374-377 (1986)

IUPAC 7th International Symposium on Cationic Polymerization and Related Processes

Dietmar Lohmann and Otto Vogl*

Technical University, Dresden
DDR-8027 Dresden, G.D.R.
and
Polytechnic Institute of New York
Brooklyn, NY 11201, U.S.A.

The 7th International Symposium on Cationic Polymerization and Related Processes, under the sponsorship of IUPAC was held from August 12 to August 15, 1985, in Jena, G.D.R. The meeting was organized by the Friedrich Schiller University in Jena and its Department of Polymer Chemistry and was under the chairmanship of Professor G. Heublein; in cooperation with Dr. M. Marek of the Institute of Macromolecular Chemistry of the Czechoslovakian Academy of Science, Prague, Czechoslovakia.

This was the first meeting in this sequence of Cationic Polymerization Symposia that was held in Eastern Europe; it was attended by over 220 participants from 16 countries, almost half of the participants were from the host country. The meeting was divided into three parts consisting of: Cationic Polymerization, Complex-Coordinative-Polymerization and Anionic Polymerization, and consisted of main lectures, lectures, communications and poster presentations.

In addition to the regular presentations some additional social activities had been planned to bring the participants closer together, to provide mechanisms of informal discussions and to learn something about the Friedrich Schiller University in Jena.

On Sunday evening, a reception was held at the University for the participants after they had arrived in town. On Monday evening, the President of the University held a reception for the main lecturers and the organizers of the meeting at the "Black Bear" restaurant which is located near the University's main building. On Tuesday a quartet recital was held in the Aula (the main auditorium) of the University. Wednesday afternoon was reserved for an excursion to the City of Jena and a sightseeing trip to Weimar, which was for centuries the seat for the Thuringian counts and also the seat of the Weimar Republic, the Capital of Germany between the First and Second World War. A visit to the Memorial of the concentration camp of Buchenwald, which is near Weimar,

Dr. Otto Vogl

Dr. Dietmar Lohmann

was also included in this program. In the evening, the reception and banquet was held at the "Fuchs Turm" Restaurant, a landmark near Jena, on top of one of the steep hills which is part of the famous Thuringian Forest; this restaurant is part of a medieval castle. The banquet included grilling of various meats outdoors; the reception and entertainment was provided by a band of hunting horn players followed by a more formal indoor banquet.

The scientific meeting was held at the Doebereiner Hall, the main lecture room of the University. It was opened by the Vice-President of the Friedrich-Schiller University, Professor Unangst who welcomed the participants of the 7th Cationic Symposium to Jena. The official representative of the IUPAC, Professor T. Saegusa of Kyoto, Japan, chairman-elect of the Division of Polymer Chemistry of the International Union for Pure and Applied Chemistry provided the greetings of IUPAC. Additional greetings were brought by the President of the Chemical Society of the G.D.R., Professor B. Philipp.

The first plenary lecture was given by Professor J. P. Kennedy, who presented his talk "A New View of Carbocationic Polymerizations." Continued research into the fundamentals of cationic olefin polymerizations led to the discovery of a family of new initiating systems that effectively induce rapid living polymerization of isobutylene under surprisingly mild conditions.

*To whom all inquiries should be addressed.

Polymer News, 1986, Vol. 11, pp. 374–377
0032-3918/86/1112-0374$10.00/0

Although truly living cationic hydrocarbon polymerization has not been achieved with the boron trichloride initiator system, chain transfer to monomer and chain termination are absent; plots of the number average molecular weight of the polymers versus the monomer concentrations were linear and could be extrapolated back to the origin. The best of the new initiating systems are boron trichloride complexes. In addition to this, homopolymerization of isobutylene, and random copolymerization of isobutylene with isoprene has also been developed. The "Structure of Active Species in the Polymerization of Lactones Initiated by Trityl Salts" was discussed by Dr. N. Manolova; in this short communication, she described the structure of the active species of several lactone polymers that have been studied by ion-trapping with triphenylphosphine; this work showed that the propagation proceeded by alkyl-oxygen bond scission and the active species were tertiary oxonium ions.

"Cationic and Coordinative Polymerization of Functional Epoxides, Olefins and Substituted Tetrahydrofurans" was the subject of Professor Otto Vogl's talk, who discussed the polymerization of functional epoxides by coordinative anionic polymerization using trialkylaluminum/water/acetylacetone systems. In some cases cationic trialkylaluminum/water systems were used. Copolymerization and terpolymerization involving functional epoxides and functional 1,3-dioxolanes with trioxane were also discussed using purely cationic initiators, such as triflic acid derivatives; classical cationic ring-opening copolymerization with substituted tetrahydrofurans was also discussed. It had been found that both the homo- and copolymerization of functionally substituted α-olefins was also possible and gave homopolymers and copolymers of functional olefins with other α-olefins and even with ethylene.

In his lecture "Ring-Opening Polymerization of Nitrogen- and Phosphorus-Containing Monomers," Professor Takeo Saegusa described four types of monomers having nitrogen, oxygen, phosphorus and even sulfur atoms in the five or six membered rings. He had shown the propagation proceeded via two different species, ionic and covalent, depending upon the counter anion which was derived from the initiator. With triflate as the anion, propagation proceeded, for cyclic phosphonium monomers, primarily by cationic propagating species, but, if for example, benzyl chloride was added to the polymerization the rate determining step was a dipol-dipol S_{N2} process.

In the afternoon, Dr. O. Nuyken, described "Detailed Studies of the Inifer Techniques." This paper is only part of numerous publications which have appeared describing the synthesis of telechelic monomers using the "inifer" technique which still has some unexplained aspects of the polymerization mechanism. Some of the questions are: a) stability of the initiator, b) interaction between the initiator and the Lewis acid (BCl_3), c) self-ionization of the Lewis acid, d) importance of transfer to initiator and e) reversibility of the termination reaction. The "Cationic Polymerization of Vinyl Ethers as Synthetic Path to Diphylic Polymers and Potential Complexants" was discussed by Professor S. Skorokhodov. Polymers with universal solubility characteristics (similar to a polymeric form of the dimethylether of ethylene glycol) were synthesized by cationic polymerization of cis-1,2-dimethyoxyethylene and/or p-dioxene. Polymers of very high molecular weight and relatively low polydispersity were obtained. Improved procedures for the cyclopolymerization of divinylethers of mono-, di-, and triethyleneglycols were also described, as were soluble crownether type polymers. Two short communications were presented from the Laboratory of Professor E. J. Goethals, involving the "Cationic Polymerization of 1,2-Disubsituted Aziridines: the "Stereochemistry of their Ring-Opening Reaction" and the "Synthesis of Polyamine Networks using Poly(1-Tertiarybutyl Aziridines)." Again, as in many other cationic polymerizations the counter anion was the triflate ion.

A most interesting invited main lecture was given by Professor S. Penczek on "Activated Monomer Propagation in Cationic Polymerization." The absence of cyclization and some unusual kinetic features of the cationic ring-opening polymerization of oxocyclic monomers conducted in the presence of active proton containing compounds (especially glycols) are the basis of this newly proposed mechanism of propagation in cationic polymerization called the "activated monomer." A predecessor of this mechanism had been known for the anionic polymerization of lactams and had also been proposed for cationic polymerization of lactams. In contrast to the usual active chain end propagation, known and accepted for classical cationic ring-opening polymerizations, this mechanism suggested that a charged monomer adds to the electrically neutral but active polymer chain end.

Professor G. Sauvet discussed the "Multiplicity of Active Centres in the Cationic Polymerization of p-Methoxystyrene." His group studied the cationic polymerization of p-methoxystyrene initiated by trityl salts in methylene chloride at various temperatures. The rate constants for initiation, propagation and chain transfer to monomer were determined. The most striking feature of this polymerization system was the apparent negative activation energy; this was attributed to an equilibrium between active species of different reactivities, the most reactive being favored at low-temperatures. "Living Cationic Polymerization of Vinyl Monomers: Mechanism and Synthesis of New Polymers" was the subject of Dr. M. Sawamoto's talk. Dr. Sawamoto of Professor Higashimuras group discussed cationic polymerization as a new route for synthesizing monodisperse "living" polymers of vinyl ethers. The scope and the mechanism of this important and novel type of living polymerization uses HI/I_2 as initiating systems and it is used for the synthesis of new block copolymers and telechelic polymers. Polymer molecular weight can be controlled by regulating monomer/initiator ratio and conversion. The monomers were primarily alkyl vinyl ethers and the polymerization proceeded not only in nonpolar but also in polar solvents such as methylene chloride. The effect of solvent polarity on the "living process" are now being investigated to clarify the dissociation state of the living ends.

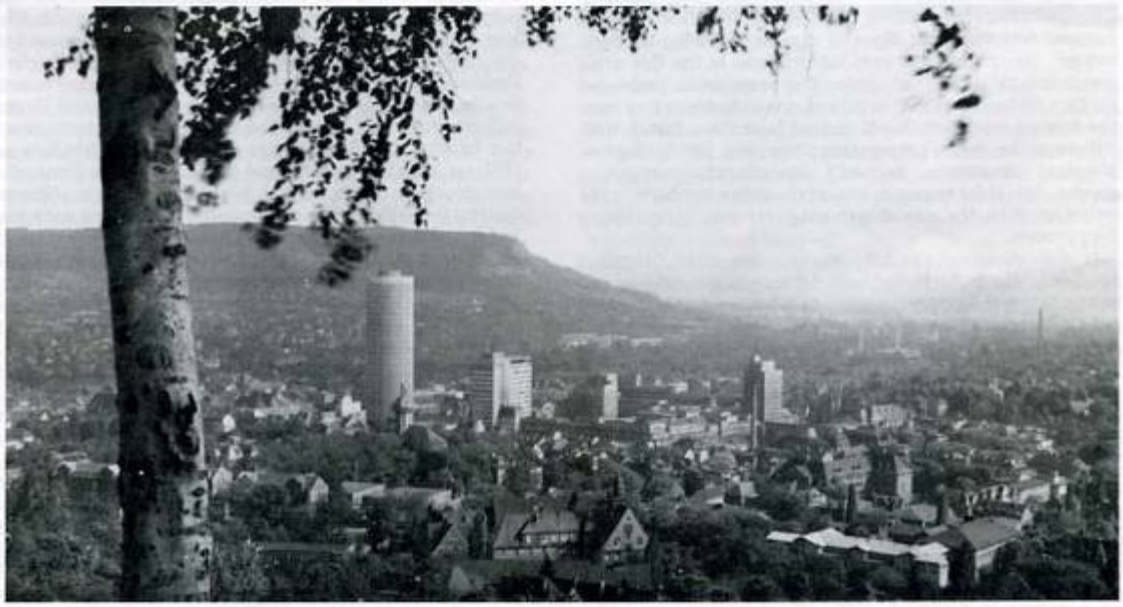
Professor R. C. Schulz presented his work on "Some New Examples of Cationic Polymerization" and discussed the synthesis and properties of cis and trans-methoxyvinyl chloride. Both monomers could be polymerized by cationic polymerization and copolymerized with styrene and 1,3-dioxolane. Ring-opening polymerization of conidine was also studied and block copolymers of styrene and conidine were prepared by a combination of anionic and cationic polymerization. "Copolymer Synthesis Using the Activated Monomer Technique" was presented by Dr. E. Franta. The cationic polymerization of cyclic acetals such as 1,3-dioxolane is known to produce cyclic oligomers besides the linear high molecular weight polymers. When the polymerization

was initiated by strong protonic acids and carried out in the presnece of a diol, hydroxy-terminated polymers were prepared without the formation of cyclic oligomers. This method of polymerizing activated monomers allowed the synthesis of various new hydroxy-terminated copolymers.

Professor T. Higashimura, was unable to attend the symposium. Dr. M. Sawamoto presented their work on "Vinyl Ethers with a Functional Group: Living Cationic Polymerization and Synthesis of Monodisperse Polymers." "Living" polymerization of vinyl monomers has thus far been confirmed for anionic polymerization processes, monomers with polar substituents have so far been difficult to polymerize under "living" conditions. Cationic polymerization of alkylvinyl ethers initiated with HI/I_2 in nonpolar media led to nearly perfect living polymers. The "living" end was protected by the large triiodide counteranion and hence HI/I_2 initiator produced living cationic polymerization conditions even when the monomer carried a polar pendant group which normally interferes with classical cationic initiation and propagation processes. For the first time, formation of living polymerization conditions were established for functional vinyl ethers which had chloroalkylphenyl ether, unsaturated vinyl or even ester pendant groups. Using such systems, block copolymers of monodisperse polyalcohols and poly(vinyl ether) macromers with methacryloyl end groups were prepared.

"Anionic Ring Opening Polymerization by Alkali Metal Solutions" was presented by Professor Z. Jedlinski. In this work, studies were carried out on the nature of the active species of alkali metal salts complexed by crownethers in such solvents such as THF. Some mechanistic aspects of the ring-opening polymerization of β-lactones and oxiranes was also discussed. "The Nature of Active Centers of Polar Monomers in Anionic Polymerization" was presented by Professor W. Berger. His group found that the nature of active centers of polar monomers in the anionic polymerization was much more complicated when functional groups were part of the monomer structure as compared to polymerizations involving only nonpolar monomers. The delocalization of the negative charge between the C-atom and the functional groups resulted in a partial intramolecular solvation of the counterion. In the copolymerization of methacrylonitrile and acrylonitrile, it was demonstrated that lithium alkoxides not only were very effective initiators, but also effective complexing agents which explained the high efficiency of the initiators. At very short reaction and very low temperatures, living polyacrylonitrile exists which could be shown by block copolymerization with methyl acrylate.

"Functionalization of Living Polymers—Results and Problems" was discussed by Dr. L. Weber. In spite of intensive research over the last few years, living polymers are specialty products which are utilized commercially in specific cases. From some of the living polymers, telechelic polymers with different functional groups at the ends of the chains could be prepared. In his laboratory, Dr. Weber studied and prepared functional telechelic polymers of α-methylstyrenes; attempts were also made to find suitable applications for these materials. The "Immortal" Anionic Ring-Opening Polymerization by Metalloporphyrin Catalysts" was discussed by Professor S. Inoue. Ring-opening polymerization of epoxides with aluminum-porphyrin–protic compounds gave polyethers where the number of the macromolecules were more than that required from the aluminum-porphyrin complex initiating systems caused by the rapid exchange between alcohol and (porphyrinato)aluminum alkoxide. The proton provides a temporary, dormant situa-



City of Jena

tion for the growing polymer; this polymerization behavior is in clear contrast with the classical and well known "living" polymerization. Professor H. R. Kricheldorf presented the work of his group on "Cationic Homo- and Copolymerization of Glycolide and Various ω-Lactones" Homo- and copolymerization of glycolide and other lactones was initiated by various methylsulfonates; methyltriflate was found to be the most effective initiator. The sequence of the addition of the individual components is essential for the optimization of both reaction time and reaction temperature. At a polymerization temperature of about 50°C copolyesters were obtained with random sequences of comonomers.

Professor H. Sumitomo presented his work on "Sterically Controlled Propagation in the Cationic Ring-Opening Polymerization of Bicyclic Acetals." In the cationic ring-opening polymerization, bicyclic acetals were always inverted at or below -78°C and gave a stereoregular polymer entirely consisting of exocyclic structural units. At higher temperatures stereoirregular polymers containing other structural unit were obtained. The ring-opening polymerization of the same cyclic monomer with conventional Lewis acid initiators has been shown to give stereoregular polyacetals which are rich in isotactic dyads. For many years, Dr. M. Marek has been involved in the work on "Complexes of Lewis Acids in the Cationic Polymerization of Olefins." He summarized his findings about the origin of donor-acceptor complexes between olefinic hydrocarbons and selected Lewis acids. Dr. Marek also studied the stoichiometry of complex formation and determined it by a variation of titrimetric methods, measurement of equilibrium constants and the establishments of thermodynamic parameters. He concluded that the complexes involved in these cases are weak and the ion-radical particles are formed by the hydrolysis of these complexes under various experimental conditions. Dr. V. A. Ponomarenko discussed his work on "Regularities of Cationic Polymerization of Substituted Aziridines." He presented some new and interesting work of his research group which is somewhat different from the work on the polymerization of aziridines that is carried out in Ghent. The work on the "Polymerization of N-Substituted Lactams" was presented by Dr. J. Sebenda. He discussed the reaction mechanism and the kinetic scheme for the polymerization of N-acyl and N-alkyllactams as well as model reaction of the corresponding dialkylamides and diacylamines with different types of initiators. The rate of polymerization proceeded via an activated monomer, which is in agreement with the electronic structure of the amide group of the lactam.

Professor J. Ulbricht discussed "The Mechanism of Ethylene/Propylene Polymerization with Supported Metal Organic Compounds." His group studied the reaction of tetrabenzylzirconium with γ-alumina. The rate of polymerization of ethylene/propylene depended on the pretreatment of the γ-alumina, and depended on the amount of tetralbenzylzirconium fixed on the support. By quenching the polymerization reaction, the concentration of active sites of the polymerization was determined. The "Determination of the Number of Active Centers in Ziegler-Natta Polymerizations of Olefins" was also the subject of a talk by Dr. J. Mejzlik. The determination of the active centers was based on a) labelling the initiating species (organometal components), b) inhibition of the polymerization, c) labelling of growing chains and d) miscellaneous experiments. Professor W. Kaminsky discussed the "Olefin Polymerization with Highly Active Soluble Zirconium Compounds. Using Aluminoxane as Cocatalyst." The final two talks were given by Professor K. Gehrke on "Polymerization of Butadiene and Styrene with Ziegler-Natta-Catalysts" and by Dr. U. Schmidt "On the Mechanism of Stereoregulation on the Allylnickel Complex Butadiene Polymerization."

Prof. Johann Wolfgang Doebereiner (1780–1849) First Chemistry Professor, University Jena

Over 60 other papers were presented as short talks or in poster form on the following three subjects: Cationic Polymerization; Coordination Polymerization and Anionic Polymerization.

This 7th Symposium on Cationic Polymerization and Related Processes has been considered by most participants as an outstanding success. It had been well organized; great attention was given by the organizers and their organizations for the proceedings of this meeting. It was decided that the next meeting on Cationic Polymerization and Related Processes, the 8th Symposium, will be held in Munich, Federal Republic of Germany, at the end of August 1987; the chairmen will be Professors R. C. Schulz and O. Nuyken.